

Estimating aerosol light scattering at the Fresno Supersite

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Abstract

Aerosol light scattering (Bsp) was estimated from particle size and chemical measurements during the winter intensive period (15 December 2000–3 February 2001) at the Fresno Supersite as part of the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS). Bsp was underestimated by 41–46% from scanning mobility particle sizer (SMPS) and optical particle counter (OPC) particle size distributions depending on assumptions about refractive index and hygroscopic growth. Bsp was underestimated by 35% using the Interagency Monitoring of PROtected Visual Environments (IMPROVE) light extinction equation and by 25% using chemical size distributions measured with micro orifice uniform deposit impactor (MOUDI) cascade impactors and a Desert Research Institute (DRI) PM_{2.5} sequential filter sampler (SFS). Underestimation of Bsp in Fresno was related to differences in the temperature and relative humidity (RH) at which various measurements were made. Evaporation of ammonium nitrate in the heated environment in which the SMPS and OPC instruments were located caused a reduction in particle size and number concentration. The MOUDI was operated outdoors at ambient temperature and RH, while a smart-heater equipped Radiance nephelometer was operated at RH < 72%. Comparing estimated and measured Bsp required adjusting the SMPS, OPC, and MOUDI size distributions to the nephelometer RH. A systematic low-bias in estimated scattering suggests that organic aerosols may have contributed to hygroscopic growth. Consistent measurement strategies are needed to properly estimate aerosol light extinction under conditions such as those found in Fresno during winter.

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1. Introduction

Pollution-derived and natural aerosols degrade visibility in urban and remote locations and play a role in climate forcing (Charlson et al., 1992). Understanding the causes and magnitudes of current and future aerosol effects on visibility and climate requires a proper understanding of their optical and hygroscopic

properties. Aerosol extinction has been inferred from satellite and ground-based remote sensing measurements (Durkee et al., 2000; Vitale et al., 2000; Hauser et al., 2005). In-situ measurements of particle size distributions and size-resolved chemistry have been used to estimate aerosol light extinction (scattering and absorption) at urban, rural, and marine locations (Hayasaka et al., 1992; Zhang et al., 1994; Lowenthal et al., 1995; Malm and Pitchford, 1997; Moosmüller et al., 1998; McInnes et al., 1998; Quinn et al., 1998, 2001; Richards et al., 1999, 2001; Hand et al., 2002; Hegg et al., 2002; Malm et al., 2003, 2005).

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Ammonium nitrate (NH_4NO_3) and organic matter dominate particle mass concentrations in California's San Joaquin Valley (SJV) during winter (Chow et al., 1993a, 1996, 2006). NH_4NO_3 is a secondary aerosol product of gaseous emissions from motor vehicle exhaust (nitrogen oxides [NO_x]) and agricultural activities (ammonia [NH_3]); it is a volatile compound that exists in the atmosphere in equilibrium with gaseous NH_3 and nitric acid (HNO_3 ; Stelson and Seinfeld, 1982; Hering and Cass, 1999). Low temperature and high relative humidity (RH) during winter favor the particle phase.

This study estimates particle light scattering (Bsp) using various methods and measurements at the Fresno Supersite (Watson et al., 2000) during the California Regional $\text{PM}_{10}/\text{PM}_{2.5}$ Air Quality Study (CRPAQS; Watson et al., 1998) winter intensive operating periods (IOPs) in late 2000 (15–18 December and 26–28 December) and early 2001 (4–7 January and 31 January–3 February). The effect of variations in theoretical assumptions and measurements on accurate estimation of Bsp is discussed.

2. Methods

The Fresno Supersite is located at 3425 First Street, approximately 5 km from the downtown district near the geographical center of the SJV. Air quality monitors are operated on the roof of a two-story building. Some instruments are located in the second-floor laboratory and draw air through rooftop inlets. Sampler inlets are located ~10 m above ground level. The following analysis uses measurements of the particle size distribution, size-resolved and $\text{PM}_{2.5}$ (particles with aerodynamic diameters $<2.5\text{ }\mu\text{m}$) chemistry, and Bsp during the CRPAQS winter IOPs.

2.1. Particle size distributions

Particle size distributions were measured with (1) a scanning mobility particle sizer (SMPS; TSI Model 3936L10, TSI, Inc., St. Paul, MN) equipped with a “long” differential mobility analyzer (DMA; TSI Model 3080, TSI, Inc., St. Paul, MN) and a condensation nucleus counter (CNC; TSI Model 3010, TSI, Inc., St. Paul, MN), and (2) an optical particle counter (OPC; Lasair 1003, Particle Measuring Systems, Boulder, CO), located in the climate-controlled laboratory. The SMPS measures

particle number concentrations (N) for particle diameters from 9 to 392 nm in 52 channels based on their electrical mobility. The OPC sizes particle diameters from 100 to 2500 nm in seven channels according to the amount of light they scatter. The SMPS and OPC approaches assume that the particles are spherical. The SMPS size distributions were corrected for multiple charging and for the decrease in small particle counting efficiency in the CNC. The OPC was factory-calibrated with polystyrene latex (PSL) beads with a refractive index of 1.59, $i0.0$. This is close to the refractive index (1.579, $i0.05$) inferred from the chemical composition of aerosol samples collected at the site (Watson et al., 2002). Hourly average size distributions were calculated from 5-min measurements. These are regarded as “quasi-dry” size distributions, since the average difference between the ambient temperature and the temperature measured in the SMPS cabinet was 17°C (Watson et al., 2002).

2.2. Size-resolved and $\text{PM}_{2.5}$ aerosol chemistry

Size-resolved chemical measurements were made under ambient conditions with micro orifice uniform deposit impactor (MOUDI) cascade impactors (MSP Corporation, Shoreview, MN). Samples were collected during CRPAQS winter IOPs from 0000 to 0500, 0500 to 1000, 1000 to 1600, and 1600 to 2400 PST (GMT-8). From 15 to 18 December, the three collocated MOUDIs were equipped with eight stages with nominal d_{50} 's (aerodynamic diameter at which 50% of particles of that size are retained by the stage) of 5.6, 2.5, 1.8, 1.0, 0.56, 0.32, 0.18, and $0.10\text{ }\mu\text{m}$, followed by an after-filter. After that time, the $1.8\text{ }\mu\text{m}$ stage was removed and a $0.056\text{ }\mu\text{m}$ stage was added. In two MOUDIs, particles were collected on clear Teflon substrates (Cadillac Plastics Co., Southfield, MI) and Teflon-membrane after-filters (Pall Sciences, R2PJ047, Ann Arbor, MI) for measurement of particle mass, elements, and water-soluble ion concentrations. The third MOUDI used pre-fired (600°C) aluminum foil substrates (MSP Corporation, Shoreview, MN) and quartz-fiber after-filters (Pall Sciences, QAT2500-VP, Ann Arbor, MI) for organic carbon (OC) and elemental carbon (EC) measurement.

$\text{PM}_{2.5}$ samples were collected on Teflon-membrane (Pall Sciences, R2PJ047, Ann Arbor, MI) and quartz-fiber (Pall Sciences, QAT2500-VP, Ann Arbor, MI) filters with Desert Research Institute (DRI; Reno, NV) sequential filter samplers (SFS)

preceded by PM_{2.5} size-selective inlets (Sensidyne Bendix 240 cyclones) and aluminum oxide tubular HNO₃ denuders (Chow et al., 1993b). Nitrate (NO₃⁻) volatilized from the quartz-fiber filters was collected on sodium chloride (NaCl)-impregnated cellulose-fiber backup filters (Whatman, 31ET, Hillsboro, OR). Samples were collected during the same time intervals as those of the MOUDIs except that two periods, 1000–1300 and 1300–1600 PST, were sampled during the MOUDI 1000–1600 PST period. Concentrations from the SFS samples during these two periods were averaged to coincide with the MOUDI sampling period.

MOUDI Teflon substrates and SFS Teflon-membrane filters were analyzed for mass by gravimetry and for elements by X-ray fluorescence (Watson et al., 1999). Water extracts of the second MOUDI Teflon substrates and SFS quartz-fiber filters were analyzed for sulfate (SO₄²⁻), NO₃⁻, and chloride (Cl⁻) by ion chromatography (IC; Chow and Watson, 1999) and NaCl-impregnated cellulose-fiber filters were analyzed for NO₃⁻ by IC ammonium (NH₄⁺) by automated colorimetry, and water-soluble sodium (Na⁺) and potassium (K⁺) by atomic absorption spectrometry. OC and EC on MOUDI aluminum foil substrates and SFS quartz-fiber filters were analyzed by thermal/optical reflectance (TOR; Chow et al., 1993c, 2005a, 2007). The optical correction for pyrolysis of OC on the SFS quartz-fiber filters was used to determine the OC/EC split for the corresponding MOUDI aluminum foil substrates. Total particulate NH₄NO₃ calculated from the sum of non-volatilized NO₃⁻ from the front filter and volatilized NO₃⁻ from the backup filter in the SFS sampler was used to estimate Bsp (Chow et al., 2005b).

2.3. Light scattering measurements

PM_{2.5} Bsp was measured at a wavelength (λ) of 530 nm using a heated nephelometer preceded by a PM_{2.5} size-selective inlet (Radiance Research Model 903, Seattle, WA). The Model 903 uses a “smart heater” which maintains RH at the nephelometer outlet below the ambient RH and does not allow it to exceed 72%. One-hour averages were calculated from 5-min Bsp measurements. The extent to which equilibrium between particles and water vapor in the nephelometer was attained is not known. If equilibrium was not reached, the particles could be larger and the indicated Bsp would be higher than expected. Conversely, heating in the nephelometer can also lead to evaporation of NH₄NO₃, a major

component of the Fresno winter aerosol (Bergin et al., 1997). This would lead to a low-bias in the measurement of Bsp.

2.4. Estimation of light scattering

Bsp, in units of Mm⁻¹, is the product of the particle concentration and its scattering cross section:

$$\text{Bsp} = \int \sigma n(D) dD, \quad (1)$$

where σ is the scattering cross section, D is particle diameter, and $n(D) dD$ is the number concentration over the diameter interval dD . σ depends on the incident light wavelength (λ), D , and the complex index of refraction (m). Eq. (1) may be reformulated as follows:

$$\text{Bsp} = \int \left[\left(\frac{3}{2D\rho} \right) Q \right] C(D) dD, \quad (2)$$

where ρ is the particle density, Q is the optical scattering efficiency, equal to $4\sigma/\pi D^2$, and $C(D) dD$ is the mass concentration over the size interval dD . The expression $[(3/2D\rho)Q]$ is the mass scattering efficiency. For spherical particles, σ and Q can be estimated using Mie theory (Mie, 1908). For particles of mixed chemical composition (e.g., inorganic ions, water), m and ρ are estimated as the volume-weighted m and ρ of the respective components. For SMPS and OPC size distribution data, it was assumed that chemical components were homogeneously mixed in particles. Mie calculations were performed per Barber and Hill (1990).

Bsp was estimated from MOUDI and PM_{2.5} SFS concentrations with the elastic light scattering interactive efficiencies (ELSIE; Sloane, 1986; Lowenthal et al., 1995) program. MOUDI stage concentrations were converted to continuous size distributions using the “Twomey Inversion” (Winklmayr et al.’s (1990) adaptation of Twomey’s (1975) nonlinear iterative algorithm). This procedure accounts for the non-ideal collection efficiencies of the MOUDI stages. ELSIE integrates discrete size distributions derived from the MOUDI concentrations, applies them over a user-specified number of size bins up to 2.5 μm , and calculates the fraction of each species mass in each bin. Species concentrations in each size bin were calculated by applying the fractional abundances to the PM_{2.5} SFS concentrations. Sulfates, nitrates, and OC and EC were assumed to be internally and homogeneously mixed. Unlike carbon and ions,

soil dust was assumed to be externally mixed because it was concentrated in the super-micron size range. SO_4^{2-} was speciated as ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, ammonium bisulfate $(\text{NH}_4\text{HSO}_4)$, or sulfuric acid (H_2SO_4) based on the molar ratios of SO_4^{2-} , NO_3^- , and NH_4^+ ions. Water associated with sulfates and nitrates was estimated using the ZSR (Zdanovskii–Stokes–Robinson) method (Stokes and Robinson, 1966) from published water activity data (Staples, 1981; Chan et al., 1992; Tang and Munkelwitz, 1994). MOUDI aerodynamic diameters were converted to geometric (Stokes) diameters based on the chemical composition, including the estimated water content, and the corresponding volume-averaged densities, in each size bin. The particle number concentration was estimated from the particle volume and the geometric mean diameter for each size bin.

A chemical extinction budget (Watson, 2002) has been used to estimate light extinction from $\text{PM}_{2.5}$ chemical concentrations measured in the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network (Malm et al., 1994, 2000). Assuming that chemical components are externally mixed, the $\text{PM}_{2.5}$ light scattering portion of this extinction budget is:

$$\text{Bsp} = 3f(\text{RH})[\text{AMSUL} + \text{AMNIT}] + 4[1.4\text{OC}] + 1[\text{Soil}]. \quad (3)$$

The concentrations ($\mu\text{g m}^{-3}$) of $(\text{NH}_4)_2\text{SO}_4$ (AMSUL) and NH_4NO_3 (AMNIT) are multiplied by a dry mass scattering efficiency of $3 \text{ m}^2 \text{ g}^{-1}$ and a hygroscopic growth factor ($f(\text{RH})$). The $f(\text{RH})$ represents the enhancement of Bsp caused by hygroscopic growth and is based on water activity data for $(\text{NH}_4)_2\text{SO}_4$ (Tang and Munkelwitz, 1994). A dry mass scattering efficiency of $4 \text{ m}^2 \text{ g}^{-1}$ is assigned to OC because of its lower density, assuming an $f(\text{RH})$ of unity. A factor of 1.4 is used to convert OC to organic compound mass (OCM; Grosjean and Friedlander, 1975; White and Roberts, 1977). This value is thought to be appropriate for urban aerosols. The $\text{PM}_{2.5}$ soil scattering efficiency [Eq. (3)] is assigned as $1 \text{ m}^2 \text{ g}^{-1}$ (Watson, 2002).

3. Results and discussion

3.1. Average size distributions

Average size distributions ($dN/d \log D$) were calculated for winter IOPs when valid and complete

(i.e., SMPS, OPC, MOUDI, nephelometer, and SFS sampler measurements) data were available. These included nine 5-h, four 6-h, and four 8-h MOUDI sampling periods. Because the MOUDI operated at ambient RH, it was necessary to adjust the MOUDI size distributions to “dry” conditions under which SMPS and OPC size measurements were made. MOUDI particle volume was estimated from chemical mass concentrations and associated water as a function of aerodynamic diameter at ambient RH. This was done in a manner similar to that of Hand et al. (2002). Water mass was estimated using water activity data for $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 from Tang and Munkelwitz (1994) and Chan et al. (1992). The MOUDI number distribution was calculated from the wet particle volume and the geometric diameter was estimated from the corresponding aerodynamic diameters and volume-average (wet) density. Densities of the individual chemical components are shown in Table 1. Geometric diameters were adjusted to dry conditions (i.e., $\text{RH} = 30\%$) from the dry particle volume and the number concentrations estimated for ambient conditions.

Average particle number distributions are shown in Fig. 1. The OPC and MOUDI distributions were similar above the first OPC channel. The MOUDI number concentrations may have diverged from the OPC below the first MOUDI stage because the inversion extrapolates the distribution in this region. SMPS concentrations were significantly lower than those of the OPC and MOUDI above $\sim 100 \text{ nm}$. Similar discrepancies reported by Watson et al. (2002) were attributed to evaporation of NH_4NO_3 from particles in or upstream of the SMPS, which was located furthest from the sampling inlet in the shelter.

Table 1
Densities and refractive indices of individual chemical components

Component	Density (g cm^{-3})	Refractive index
Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$	1.76	1.53, i0.0
Ammonium nitrate (NH_4NO_3)	1.73	1.55, i0.0
Organic Compound Mass (OCM)	1.2	1.55, i0.0
Elemental carbon (EC)	1.7	1.9, i0.6
Soil	2.3	1.56, i0.005
Water	1.0	1.33, i0.0

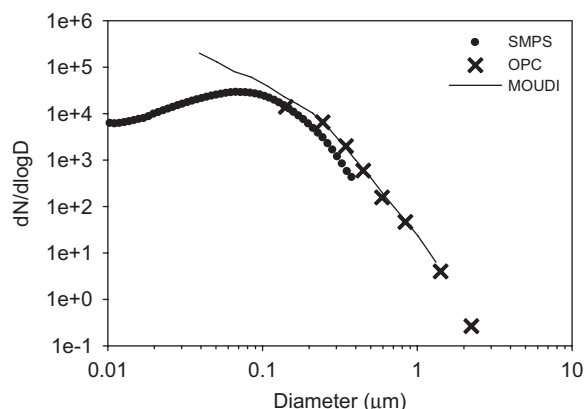


Fig. 1. Average particle number distributions ($dN/d \log D$) derived from scanning mobility particle sizer (SMPS), optical particle counter (OPC), and micro orifice uniform deposit impactor (MOUDI) measurements in Fresno from 26 to 28 December 2000, 4 to 7 January 2001, and 31 January to 3 February 2001. MOUDI geometric (Stokes) diameters were adjusted to relative humidity (RH) = 30%.

3.2. Estimation of Bsp

3.2.1. Using the particle size distributions

Based on the results in Fig. 1, which shows lower-than-expected SMPS concentrations above 100 nm, SMPS concentrations from 9 to 100 nm and OPC concentrations from 100 to 2500 nm were used. $PM_{2.5}$ Bsp was estimated from 273 hourly average SMPS and OPC size distributions using two approaches. In Case 1, the refractive index of all particles was assumed to be 1.6, $i0.05$, a value similar to that (1.579, $i0.05$) inferred from average $PM_{2.5}$ chemical composition during winter (Watson et al., 2002). No attempt was made to account for hygroscopic growth that may have occurred in the heated nephelometer. Fig. 2 compares estimated and measured Bsp assuming a uniform refractive index and no hygroscopic growth. The average error (AE) is used as a metric for comparing estimated and measured Bsp:

$$AE(\%) = 100\% \sum_{i=1}^N \frac{\text{Estimated Bsp} - \text{Measured Bsp}}{\text{Measured Bsp}} \quad (4)$$

While Bsp was underestimated by 46%, on average, in Case 1, estimated and measured Bsp were highly correlated ($R^2 = 0.94$).

In Case 2, each hourly average size distribution was characterized by the chemical composition of

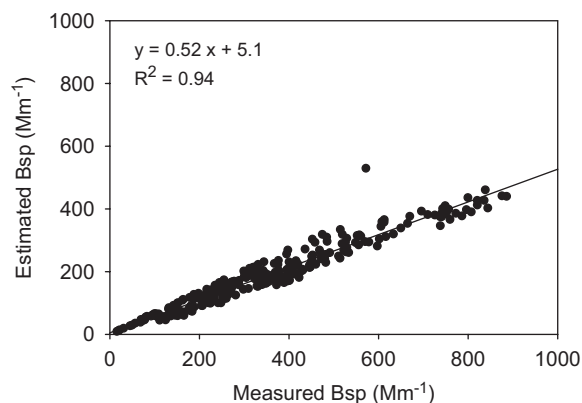


Fig. 2. Comparison between estimated and hourly average measured $PM_{2.5}$ Bsp. Bsp estimated from measured scanning mobility particle sizer (SMPS) and optical particle counter (OPC) size distributions with an assumed refractive index of 1.6, $i0.05$ and no hygroscopic growth (Case 1 approach).

the corresponding $PM_{2.5}$ SFS sample. SO_4^{2-} and NO_3^- were assumed to be present as $(NH_4)_2SO_4$ and NH_4NO_3 , respectively, based on the concentrations of SO_4^{2-} , NO_3^- , and NH_4^+ ions. The average molar ratio of $PM_{2.5}$ SFS NH_4^+ to the sum of SO_4^{2-} and NO_3^- was 1.06 ± 0.05 . OCM was estimated assuming an OCM/OC ratio of 1.4 (Grosjean and Friedlander, 1975; White and Roberts, 1977; Watson, 2002). $PM_{2.5}$ soil mass was estimated as a modified sum of metal oxides (Malm et al., 2000):

$$\text{Soil} = 2.2Al + 2.49Si + 1.63Ca + 2.42Fe + 1.94Ti. \quad (5)$$

Water was added to particles using water activity data for $(NH_4)_2SO_4$ and NH_4NO_3 from Tang and Munkelwitz (1994) and Chan et al. (1992), respectively, at the hourly average RH measured in the nephelometer (Lowenthal et al., 2000). Therefore, all particle diameters were increased by the same growth factor. OCM was assumed to be non-hygroscopic (Malm et al., 2000). The volume-weighted average refractive index was calculated from the densities and refractive indices of the individual chemical components and water, as shown in Table 1.

Fig. 3 shows that estimated and measured Bsp were again highly correlated ($R^2 = 0.95$) but Bsp was underestimated by 41%, on average. The estimated average Bsp was 10% higher in Case 2 ($203 Mm^{-1}$) than in Case 1 ($185 Mm^{-1}$). The average RH measured in the heated nephelometer was 56%. The corresponding estimated average increase in particle diameter due to hygroscopic

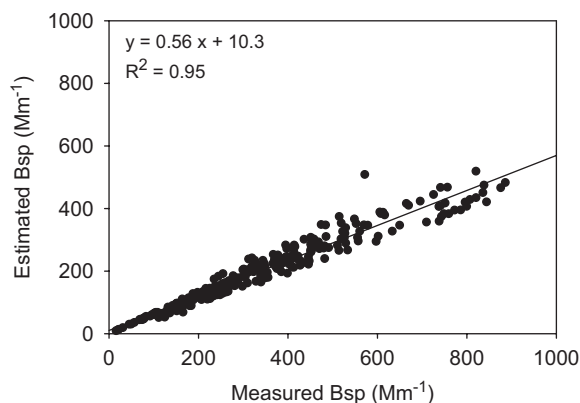


Fig. 3. Comparison between estimated and hourly average measured $\text{PM}_{2.5}$ Bsp. Bsp estimated from measured scanning mobility particle sizer (SMPS) and optical particle counter (OPC) size distributions with refractive index and hygroscopic growth estimated from $\text{PM}_{2.5}$ SFS chemistry (Case 2 approach).

growth was 7%. For a given refractive index, larger particles in the sub-micron size range should lead to more Bsp. However, since water has a lower refractive index (1.33, i0.0) than the other chemical components, the volume-weighted average refractive index of hydrated particles in Case 2 (1.54, i0.04) was lower than that used in Case 1 (1.6, i0.05). For a given particle size, a lower refractive index should produce less light scattering. The combined effect of increased particle size and lower refractive index in Case 2 resulted in a relatively small increase in estimated light scattering compared with Case 1.

3.2.2. Using MOUDI size-resolved chemistry

$\text{PM}_{2.5}$ Bsp estimated from MOUDI and $\text{PM}_{2.5}$ SFS chemical concentrations is compared with measured Bsp in Fig. 4. Stokes diameters estimated for the MOUDI at ambient RH were adjusted to the lower RH measured in the nephelometer, as described above. In this case, Bsp was underestimated by 25%, on average. The correlation between estimated and measured Bsp was high ($R^2 = 0.89$), even though there were far fewer observations ($N = 19$) than in Case 1 or Case 2 ($N = 273$). The slope of the regression of estimated on measured Bsp (0.74) was higher than those in Case 1 (0.52) and Case 2 (0.56). While the MOUDI and OPC distributions were similar, as shown in Fig. 1, the MOUDI particle number concentration for dry diameters $> 100 \text{ nm}$ was 9780 cm^{-3} . This value is higher than that derived for Case 2 (6217 cm^{-3}), which explains why more scattering was estimated from the MOUDI concentrations.

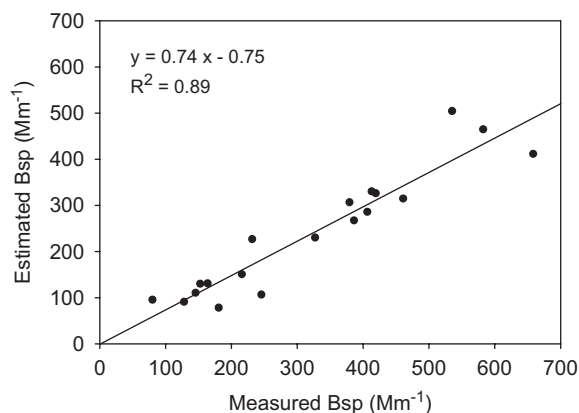


Fig. 4. Comparison between estimated and measured $\text{PM}_{2.5}$ Bsp from micro orifice uniform deposit impactor (MOUDI) size distributions and $\text{PM}_{2.5}$ sequential filter sampler (SFS) chemistry (MOUDI approach).

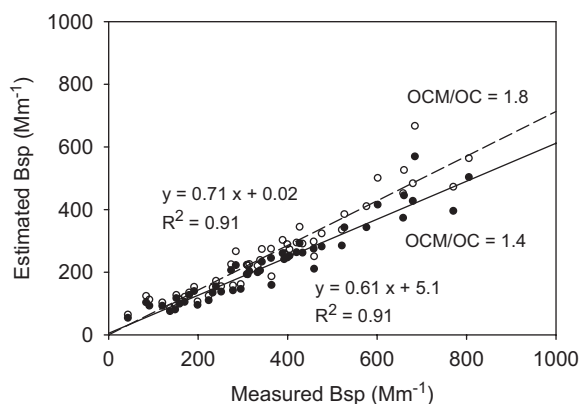


Fig. 5. Comparison between estimated and measured $\text{PM}_{2.5}$ Bsp from $\text{PM}_{2.5}$ sequential filter sampler (SFS) chemistry using the IMPROVE equation. Closed circles are $\text{OCM/OC} = 1.4$; open circles are $\text{OCM/OC} = 1.8$. OCM is organic compound mass, including species other than carbon such as oxygen and hydrogen (IMPROVE approach).

3.2.3. Using the IMPROVE equation

$\text{PM}_{2.5}$ Bsp was estimated from $\text{PM}_{2.5}$ SFS chemical concentrations using the IMPROVE equation [Eqs. (3) and (5)]. There were 48 SFS samples with corresponding Bsp measurements during the CRPAQS IOPs. The $f(\text{RH})$ in Eq. (3) were calculated for each hourly average RH measured in the nephelometer and these were averaged for the corresponding SFS sampling periods. As shown in Fig. 5, Bsp was underestimated by 35% assuming an OCM/OC ratio of 1.4. The slope of the regression of estimated on measured Bsp was 0.61 with a correlation (R^2) of

0.91. Malm et al. (2005) conducted a study at Yosemite National Park during summer 2002, when the aerosol was influenced by fresh and aged natural fire smoke. Based on mass closure analysis, they concluded that an OCM/OC ratio of 1.8 was more realistic than the typical urban value of 1.4 under these conditions. Applying the IMPROVE equations with an OCM/OC ratio of 1.8 to Fresno concentrations, Bsp was underestimated by 26% and the slope increased to 0.71 (Fig. 5).

PM_{2.5} mass closure was investigated, with reconstructed mass equal to the sum of PM_{2.5} SO₄²⁻ as (NH₄)₂SO₄, NO₃⁻ as NH₄NO₃ (based on the front quartz-fiber filter non-volatilized NO₃⁻ concentration), OCM, EC, and soil [calculated from Eq. (5)]. Reconstructed and measured PM_{2.5} concentrations are compared in Fig. 6. With OCM/OC ratios of 1.4 and 1.8, PM_{2.5} mass was over-estimated by 4.5% and 18.9%, on average, respectively. In both cases, R^2 between reconstructed and measured mass was ≥ 0.98 . The slopes and intercepts were 0.80 and 8.1 $\mu\text{g m}^{-3}$ for OCM/OC of 1.4 and 0.93 and 8.2 $\mu\text{g m}^{-3}$ for OCM/OC of 1.8, respectively. However, these results are not definitive with respect to determining the OCM/OC ratio in Fresno. Table 2 shows that AE [Eq. (4)] varies considerably with PM_{2.5} concentration, whether the OCM/OC ratio is 1.4 or 1.8.

3.3. Systematic underestimation of Bsp

Comparisons between estimated and measured PM_{2.5} Bsp using the four different approaches are

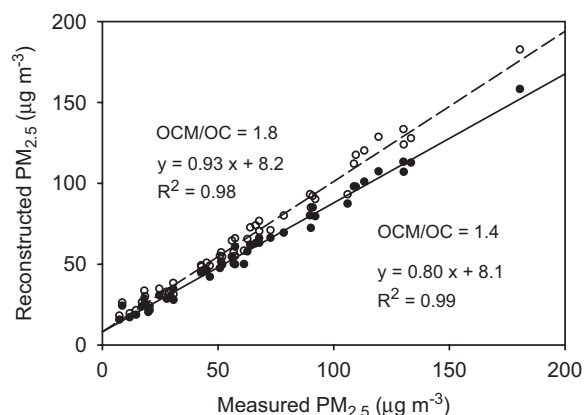


Fig. 6. Comparison between reconstructed and measured PM_{2.5} mass concentration. Closed circles are OCM/OC = 1.4; open circles are OCM/OC = 1.8. OCM is organic compound mass, including species other than carbon such as oxygen and hydrogen.

Table 2

Average error (AE; %) in reconstructed PM_{2.5} mass as a function of measured PM_{2.5} mass for OCM/OC^a = 1.4 and 1.8

PM _{2.5} mass ($\mu\text{g m}^{-3}$)	AE (%) (OCM/OC = 1.4)	AE (%) (OCM/OC = 1.8)
<20	67	90
20–40	3.2	16.5
40–80	–3.4	8.5
60–80	–8.6	4.5
80–100	–13.1	–1.2
>100	–34	0.40

^aOC, organic carbon; OCM, organic compound mass.

summarized in Table 3. Bsp was consistently underestimated by all of the approaches examined. In rank order, the AEs were –25% for the MOUDI approach, –26% and –35% for the IMPROVE approach (assuming an OCM/OC ratio of 1.8 and 1.4, respectively), –41% for Case 2, and –46% for Case 1. Watson et al. (2002) estimated Bsp in Fresno using SMPS data for diameters up to 400 nm. Bsp was underestimated for the winter of 2000–2001 but not for the following summer. Underestimation during winter was attributed to evaporation of NH₄NO₃ in or preceding the SMPS in the heated shelter. During summer, most NO₃⁻ was present as gaseous HNO₃ and there was little difference between the shelter and ambient temperatures (Watson et al., 2002; Chow et al., 2005b).

In Case 2, OPC data were used for particles >100 nm; this size range accounted for >99% of the estimated light scattering. While Bsp was underestimated to a lesser extent in Case 2 than by Watson et al. (2002), OPC size distributions during winter may also have been affected by evaporation of NH₄NO₃ in the heated shelter. However, evaporation of NH₄NO₃ did not account for underestimation of Bsp in the MOUDI or IMPROVE approaches, which were based on PM_{2.5} SFS total particulate NO₃⁻.

A possible cause of underestimation of Bsp is examined in Fig. 7, which compares RH in the nephelometer with AE for: (a) the Case 2 approach (Fig. 3), (b) the MOUDI approach (Fig. 4), and (c) the IMPROVE approach (Fig. 5). It is apparent that underestimation of Bsp increased with increasing RH in Case 2 (Fig. 7a). A similar relationship is suggested for the MOUDI approach (Fig. 7b), although the correlation was not significant. There was no relationship for the IMPROVE approach (Fig. 7c). The Case 2 and MOUDI results

Table 3

Comparisons between estimated and measured PM_{2.5} Bsp using four different approaches

	Case 1 ^a	Case 2 ^b	MOUDI ^c	IMPROVE (OCM/OC = 1.4) ^d	IMPROVE (OCM/OC = 1.8) ^e
Average estimated Bsp (Mm ⁻¹)	185.0	203.3	239.2	222.8	255.8
Average measured Bsp (Mm ⁻¹)	345.2	345.2	322.3	358.7	358.7
Average error (%)	-46	-41	-25	-35	-26
Number of cases	273	273	19	48	48

^aBsp estimated from particle size distribution measured with the SMPS and OPC. The refractive index of all particles was assumed to be 1.6, i0.05 and no attempt was made to account for hygroscopic growth.

^bBsp estimated from particle size distribution measured with the SMPS and OPC. The refractive index and hygroscopic growth factors were based on the corresponding PM_{2.5} SFS filter chemical composition. Organics assumed to be non-hygroscopic.

^cBsp estimated from MOUDI size distributions applied to PM_{2.5} SFS filter chemical composition. Refractive index and hygroscopic growth estimated as a function of size and chemical composition. Organics assumed to be non-hygroscopic.

^dBsp estimated from the PM_{2.5} SFS filter chemical composition using the IMPROVE equations [Eqs. (3) and (5)] with OCM/OC = 1.4. Organics assumed to be non-hygroscopic.

^eBsp estimated from the PM_{2.5} SFS filter chemical composition using the IMPROVE equations [Eqs. (3) and (5)] with OCM/OC = 1.8. Organics assumed to be non-hygroscopic.

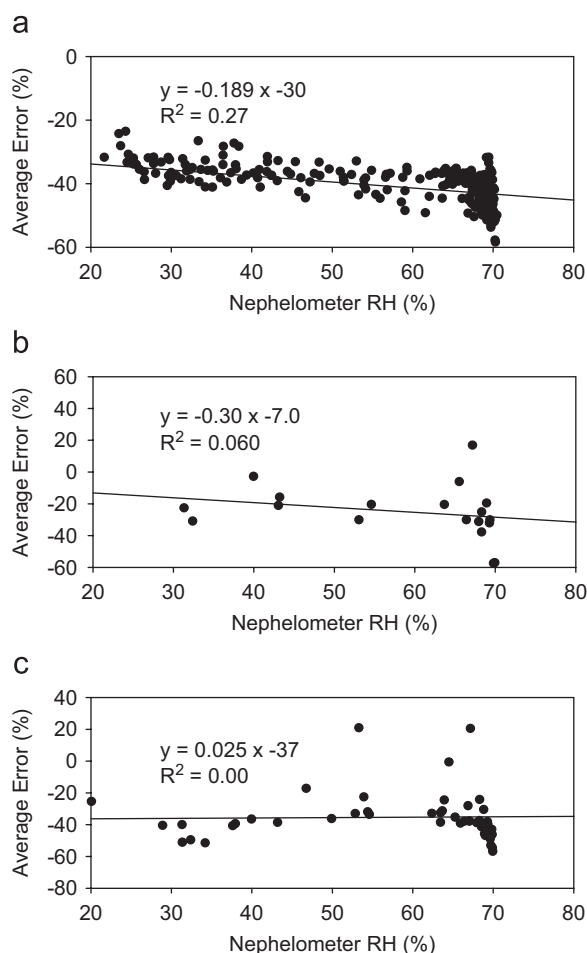


Fig. 7. Relationship between relative humidity (RH in %) in the nephelometer and the average error (%) for (a) Case 2 approach (Fig. 3); (b) MOUDI approach (Fig. 4); (c) IMPROVE approach (Fig. 5).

(Fig. 7a and b) suggest that hygroscopic growth as a function of RH was underestimated. This may not be evident in the IMPROVE approach, which assumes constant values for dry scattering efficiencies. Lowenthal and Kumar (2004) demonstrated that this assumption may not be valid at remote IMPROVE sites, where scattering efficiencies vary with mass concentration and particle size.

All of the approaches assume that OCM is not hygroscopic. However, there is evidence that organics may account for an important fraction of aerosol hygroscopic growth (Saxena and Hildemann, 1997; Gysel et al., 2004; Speer et al., 2003; Dinar et al., 2006, 2007). Assuming that OCM and NH₄NO₃ absorb the same amount of water per unit concentration and that the OCM/OC ratio is 1.4, AE in the MOUDI approach would be reduced from -25% to -19%. If a similar assumption is made for the IMPROVE approach and the $f(RH)$ term is applied to OCM ($1.4 \times OC$), AE is reduced from -35% to -10%. Additional hygroscopic growth by organics will increase estimated Bsp.

4. Conclusions

Particle light scattering (Bsp) was estimated from particle size and chemical measurements during the CRPAQS winter IOPs from 15 December 2000 to 3 February 2001 at the Fresno Supersite and compared with Bsp measured with a Radiance model 903 nephelometer. The nephelometer heated the air stream, which lowered the RH in the instrument with respect to ambient RH to <72%. Bsp estimated from particle size distributions measured

with a SMPS and an OPC was underestimated by 46% when a constant refractive index (1.6, $i0.05$) and no hygroscopic growth was assumed (Case 1) and by 41% when refractive index and hygroscopic growth were estimated from $PM_{2.5}$ SFS chemical concentrations (Case 2). Bsp was underestimated by 35% using the IMPROVE light extinction equation and by 25% using chemical size distributions measured with MOUDI cascade impactors and $PM_{2.5}$ SFS concentrations.

The underestimation of Bsp in Fresno appears to be related to differences in the conditions under which the various measurements were made. The continuous particle sizing instruments were operated in a temperature-controlled laboratory which led to evaporation of NH_4NO_3 and reduction in particle size and possibly number concentration. The MOUDI was operated outdoors at ambient temperature and RH. The nephelometer was also operated outdoors at lower-than-ambient RH. To reconcile differences in measurement conditions in the estimation of Bsp, it was necessary to “adjust” the SMPS, OPC, and MOUDI size distributions to the nephelometer RH. This required assumptions about the relationship between aerosol chemical composition and hygroscopic growth that may not have been accurate, in part because of the potential role of organics in hygroscopic growth. These results demonstrate that measurement consistency is an important consideration for experimental studies of aerosol light extinction. In addition, a better understanding of organic composition and hygroscopicity is needed for locales like Fresno where OC is a major component of the aerosol.

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